Articles

Reaction of the Ruthenium(II) Indenyl Complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ with Terminal Alkynes. Mechanisms of 1-Alkyne to η^1-Vinylidene Transformation and Kinetic Detection of Hemilability of the Allylphosphine Ligand

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The reaction of the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ (**1**) with $p\text{-}XC_6H_4C{\equiv}CH$ (X = H, Cl) yields the transient and observable vinylidene species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)(=C{=}CH(p\text{-}XC_6H_4))]^+$, which react further by an intramolecular [2 + 2] cycloaddition process, forming bicyclic alkylidene compounds. The formation of the vinylidene intermediates, associated with a change of the binding mode of the allylphosphine ligand from κ^3(P,C,C) to monodentate κ^1(P) coordination, has been investigated by kinetic measurements carried out in chloroform-*d* at 38 °C. Plots of first-order k_{obs} values vs concentration of arylalkyne are linear with a positive intercept on the *y* axis. The reaction proceeds via two parallel pathways, one which is first order in complex **1** and first order in arylalkyne, second order overall, and one which is zero order in arylalkyne, overall first order. The second-order pathway implies rate-determining nucleophilic attack of the arylalkyne on complex **1**, $k_2 = [5.5(\pm0.4)] \times 10^{-4}$ (X = H) and $[2.8(\pm0.3)] \times 10^{-4}$ M^{-1} s^{-1} (X = Cl) being the corresponding rate constants, associated with displacement of the allylic double bond or a haptotropic shift of the indenyl ring. The first-order pathway involves rate-determining formation of a transient 16-electron intermediate arising from complex **1** by reversible decoordination of the allylic double bond and rapid reaction with the incoming arylalkyne. The rate of this route is independent of the concentration and nature of the alkyne ($k_1 = [9.5(\pm2.5)] \times 10^{-5}$ s^{-1} for X = H; $[6.9(\pm1.5)] \times 10^{-5}$ s^{-1} for X = Cl) and corresponds to the rate of formation of the intermediate species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]^+$. The vinylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}RR')\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][BF_4]$ (R′ = H, R = Ph (**3a**), *p*-MeC_6H_4 (**3b**), *p*-ClC_6H_4 (**3c**); R′ = Me, R = Ph (**4a**), *p*-MeC_6H_4 (**4b**)) have been independently synthesized by electrophilic attack of HBF_4 or $MeSO_3CF_3$ on the alkynyl derivatives $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2(CH_2\text{-}CH{=}CH_2)\}(PPh_3)]$ (R = Ph (**2a**), *p*-MeC_6H_4 (**2b**), *p*-ClC_6H_4 (**2c**)), obtained in turn from $[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$.

Introduction

The transformation of terminal alkynes into ruthenium cumulenylidene derivatives represents a convenient method of alkyne functionalization,[1] as well as a direct access into metal−vinylidene species (eq 1).[2]

$$RC{\equiv}CH + RuL_n \rightleftharpoons Ru(=C{=}CHR)L_{n-1} + L \quad (1)$$

These compounds are extremely useful for catalytic reactions[3] or for further synthetic elaboration of the organic fragment.[4]

The interaction of the 1-alkyne with the metal complex involves first the formation of an η^2 adduct, which

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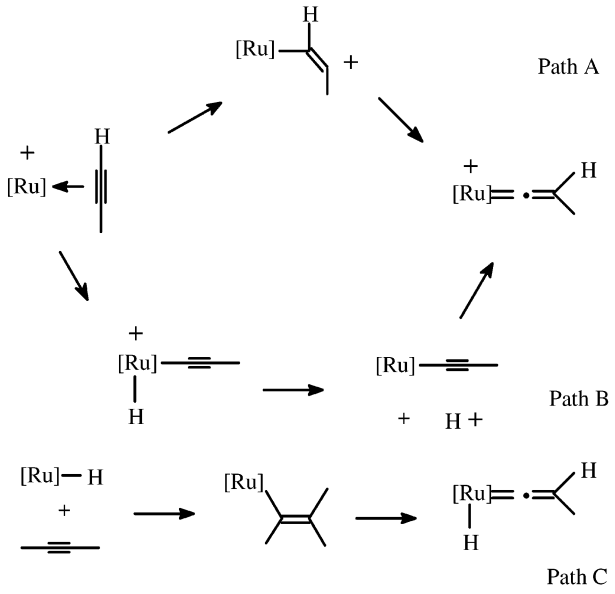
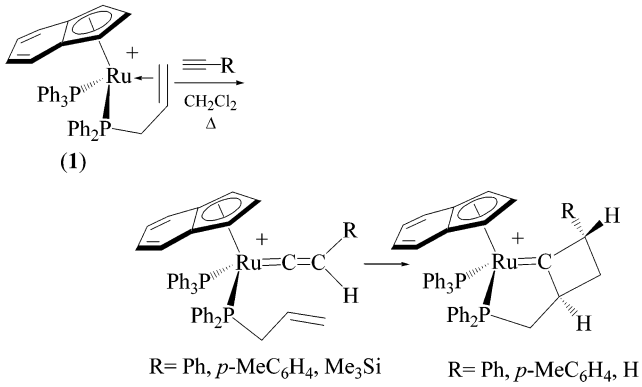
Scheme 1



rearranges into an η^1-vinylidene species. Various mechanisms have been proposed for this tautomerization process (Scheme 1). In most cases, the η^2 adduct moves toward a σ-η^1 coordination, which is followed by a 1,2-hydrogen shift (path A).[5] In the reaction of the complex [Ru(η^5-C_5Me_5)Cl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) with terminal alkynes, the hydrido−alkynyl complexes [RuH(η^5-C_5Me_5)(C≡CR)(dippe)] have been isolated and shown to be intermediates in the subsequent formation of the η^1-vinylidene compounds.[6] The process occurs by proton dissociation from ruthenium and protonation at the β-carbon atom (path B). In the case of ruthenium hydride complexes, the reaction of [RuHX(H_2)(P^tBu_2Me)$_2$] (X = Cl, I) proceeds by an alternative mechanism involving insertion of the alkyne into the Ru−H bond to form a vinyl species, which changes into a hydrido vinylidene complex by a hydrogen shift from carbon(1) to ruthenium (path C).[7] In the description of a novel synthetic route to functionalized terminal alkynes from the corresponding η^1-vinylidene ruthenium complexes, ab initio molecular orbital calculations have been reported on the η^2-alkyne/η^1-vinylidene tautomerization proceeding through a 1,2-hydrogen shift mechanism, for the model structure [Ru(η^5-C_9H_7)(PH_3)$_2$(η^2-HC≡CH)].[8] Several theoretical studies have dealt with this η^2/η^1 rearrangement,[5,7−9] and some kinetic experiments have been reported.[6,10] A specific point addressed in this work regards instead the initial interaction of the free alkyne with the metal

Scheme 2. Reaction of Complex 1 with Terminal Alkynes



complex and the mechanisms by which the metal center can be accessed.

We have recently described that the complex [Ru(η^5-C_9H_7){κ^3(*P*,*C*,*C*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][PF_6] (**1**) reacts with RC≡CH (R = Ph, *p*-MeC_6H_4, $SiMe_3$), yielding bicyclic compounds containing a cyclobutylidene ring (Scheme 2).[11a,b] It has been proved that the reaction proceeds through the formation of vinylidene intermediates which undergo an intramolecular [2 + 2] cycloaddition of the allylic and vinylidene C−C double bonds. This reaction stems from the presence in the precursor complex **1** of allylphosphine, $PPh_2(CH_2CH{=}CH_2)$, which acts as a hemilabile κ^3(P,C,C) ligand, allowing the π-coordination of the incoming alkyne and subsequent tautomerization to afford the vinylidene species.

Hybrid hemilabile ligands are gaining increasing relevance in coordination and organometallic chemistry,[12] since they can reversibly create and/or occupy a vacant coordination site at the metal, with consequent stabilization of reactive intermediates or enhancement of reactivity in catalytic reactions.[12c] The chemistry of ruthenium complexes containing hemilabile ligands is well documented.[13] One key feature of the hybrid phosphine−olefin ligands is in fact the presumed ability to easily dissociate the C−C double bond and allow interaction between the metal center and the organic

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substrate. The specific hemilabile character of $PPh_2(CH_2CH{=}CH_2)$ in the indenyl complex **1** has been shown in the reactions with nitriles, which yield the cationic complexes $[Ru(\eta^5\text{-}C_9H_7)(N{\equiv}CR)\{\kappa^1(P)\text{-}Ph_2P(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ (R = Me, benzyl), featuring a P-monodentate coordination of allylphosphine.[14] In the same context, the reactions of the Cp* complex $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^1(P)\text{-}PPh_2CH_2CH{=}CH_2\}\{\kappa^3(P,C,C)\text{-}PPh_2CH_2CH{=}CH_2\}][PF_6]$ with two-electron ligands (L), yielding monodentate phosphine−allyl complexes $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^1(P)\text{-}PPh_2CH_2CH{=}CH_2)\}_2L][PF_6]$, occur readily through substitution of the coordinated olefin.[13c]

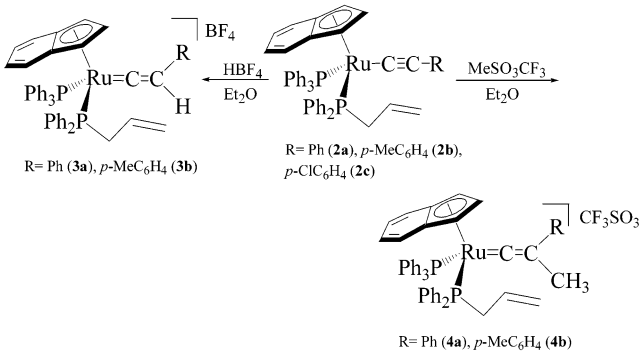
We report here on the reaction of the complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ with terminal alkynes and, in particular, on rate measurements for the first step of Scheme 2, in which the corresponding η^1-vinylidene complex is formed. The kinetic study is focused on the specific role of the allylphosphine ligand, as a bidentate hemilabile donor system, in the mechanism of the 1-alkyne/vinylidene transformation (eq 1). To identify the intermediate species observed in the kinetics, the synthesis and characterization of the vinylidene complexes are also reported. Part of the synthetic work here presented has been reported in a preliminary communication.[11a]

Results and Discussion

Although terminal alkynes are appropriate sources of the vinylidene group in metal complexes, the reaction of complex **1** with terminal alkynes yields cycloaddition products (Scheme 2).[11] Therefore, we devised an alternative synthetic procedure to obtain vinylidene derivatives via protonation of alkynyl precursors, thus avoiding the consecutive cycloaddition reaction.

Synthesis of the Alkynyl Complexes $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$ (R = Ph (2a), *p*-MeC_6H_4 (2b), *p*-ClC_6H_4 (2c)). Treatment of $[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^1(P)\text{-}Ph_2P(CH_2CH{=}CH_2)\}(PPh_3)]$[14] with terminal alkynes and KOH in methanol allows, after chromatographic workup, the isolation of the alkynyl derivatives $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$ (R = Ph (**2a**), *p*-MeC_6H_4 (**2b**), *p*-ClC_6H_4 (**2c**)) as yellow air-stable solids (80−95% yields). The alkynyl complexes can be also obtained by reaction of $[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$ with the terminal alkyne in the presence of KO*t*Bu in refluxing dichloromethane. Complexes **2a**,**b** were characterized by elemental analyses and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra show two doublet resonances in the ranges δ 44.1−43.5 and 53.2−53.5 ppm, in accord with the expected AB system arising from the inequivalent phosphorus nuclei of the two monodentate phosphines. The ^1H and $^{13}C\{^1H\}$ NMR spectra confirm the $\kappa^1(P)$ coordination mode of allylphosphine, displaying resonances of the uncoordinated allylic group: (i) two $=CH_2$ resonances at δ 3.97 and 4.61 ppm (**2**) or δ 3.56 and 4.45 ppm (**2b**) and one =CH at δ 4.71 ppm (**2a**) or δ 4.57 ppm (**2b**) in the ^1H NMR spectra; (ii) resonances of $=CH_2$ at δ 119.8 ppm (d, J_{CP} = 8.4 Hz, **2a**) or δ 121.9 ppm (s, **2b**) and of =CH at δ 123.2 ppm (**2a**) or δ 127.5 ppm (**2b**) in the $^{13}C\{^1H\}$ NMR spectra. Alkynyl C_α and C_β resonances are found at δ 89.9 (br s) and 109.8 ppm (**2a**) or at δ 73.9 (d, J_{CP} = 20.5 Hz) and 92.9 (**2b**). All attempts to obtain **2c** with analytical purity have failed, including those samples obtained by the reaction of the parent complex with *p*-$ClC_6H_4C{\equiv}CH$ and KO^{t}Bu in refluxing dichloromethane. Nevertheless, spectroscopic characterization has been obtained from IR and NMR data. The most significant features are as follows: (i) two $=CH_2$ resonances at δ 3.90 and 4.62 ppm and one =CH at δ 4.57 ppm in the ^1H NMR spectrum; (ii) resonances of the olefinic groups $=CH_2$ at δ 118.2 ppm and =CH at δ 122.5 ppm and C_α and C_β resonances at δ 92.0 (br s) and 113.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

Scheme 3. Independent Synthesis of the Vinylidene Complexes $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(R)H\}\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][BF_4]$ and $[Ru(\eta^5\text{-}C_9H_7)\{(C{=}C{=}R(Me)\}\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][CF_3SO_3]$



Synthesis of the Vinylidene Complexes $[Ru\{{=}C{=}CR(R')\}(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][BF_4]$ (R′ = H, R = Ph (3a), *p*-MeC_6H_4 (3b); R′ = Me, R = Ph (4a), *p*-MeC_6H_4 (4b)). The treatment of a solution of the alkynyl derivatives **2a**,**b** in diethyl ether with $HBF_4{\cdot}Et_2O$ at room temperature leads to the precipitation of a solid identified as the vinylidene complexes $[Ru\{{=}C{=}CR(H)\}(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][BF_4]$ (R = Ph, (**3a**), *p*-MeC_6H_4 (**3b**)) in 80−95% yields. Similarly, the vinylidene derivatives $[Ru\{(C{=}C{=}R(Me)\}(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][CF_3SO_3]$ (R = Ph (**4a**), *p*-MeC_6H_4 (**4b**)) are obtained in 85−90% yields from **2a**,**b** by the addition of $MeSO_3CF_3$ (Scheme 3). However, the addition of $HBF_4{\cdot}Et_2O$ at room temperature to a solution of **2c** in diethyl ether leads to decomposition products. Complexes **3a**,**b** and **4a**,**b** have been isolated as air-stable brown solids and characterized by elemental analysis and spectroscopic methods. The IR spectra show strong $\nu(BF_4)$ (1055−1063 cm^{-1}) and $\nu(CF_3SO_3)$ (1198−1203 cm^{-1}) absorptions along with a weak ν(C=C) band at 1628−1641 cm^{-1}. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data support the presence of the vinylidene group. In particular, $^{13}C\{^1H\}$ NMR spectra show the characteristic low-field C_α and C_β resonances at respectively δ 360.1 and 116.1 ppm (**3a**), δ 369.2 and 117.2 ppm (**3b**), δ347.6 and 117.3 ppm (**4a**), and δ 348.4 and 121.9 ppm (**4b**). ^1H NMR spectra exhibit the expected peaks arising from the proton of the vinylidene group at δ 5.34 (**3a**) and 5.31 ppm (**3b**) as broad signals and those of the methyl group, which appear as singlet signals at δ 2.40 (**4a**) and 1.92 ppm (**4b**).

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Reactions of Ru(η^5-C_9H_7){κ^3(*P,C,C*)-$PPh_2(CH_2$-$CH{=}CH_2$)}(PPh_3)][PF_6] (1) with Terminal Alkynes. Complex **1** reacts with an excess of phenylacetylene or *p*-tolylacetylene, in dichloromethane at reflux, to give the corresponding bicyclic alkylidene compound [Ru(η^5-C_9H_7){κ^2(*P,C*)-(=CC(R)$HCH_2CHCH_2PPh_2$)}(PPh_3)][PF_6] (R = Ph, *p*-MeC_6H_4). The complex obtained from the reaction with PhC≡CH has been fully characterized by X-ray analysis.[11a] The reaction with (trimethylsilyl)-acetylene in the presence of NH_4PF_6 affords [Ru(η^5-C_9H_7){κ^2(*P,C*)-(=$CCH_2CH_2CHCH_2PPh_2$)}(PPh_3)][PF_6] (85%), in which the acidic ammonium ion has assisted the protodemetalation of the C−Si bond.[15] To get information on the possible steps leading to the cycloaddition products, the reactions of complex **1** with PhC≡CH, $Me_3SiC{\equiv}CH$, and *p*-$ClC_6H_4C{\equiv}CH$ in chloroform-*d* have been monitored at 38.1 °C by ^1H and $^{31}P\{^1H\}$ NMR until completion. A large excess of the alkyne with respect to the ruthenium complex was used in order to ensure pseudo-first-order conditions and allow us to obtain rate data. In the $^{31}P\{^1H\}$ NMR spectra, the disappearance of the two doublets of complex **1** (δ 55.1 and − 69.8 ppm; ^2J = 35 Hz)[14] is accompanied by the formation of two doublets at δ 43.9 and 32.7 ppm (^2J = 25 Hz) in the case of the reaction with PhC≡CH and of two doublets at δ 43.8 and 32.8 ppm (^2J = 24 Hz) in the case of *p*-$ClC_6H_4C{\equiv}CH$, indicating the formation of the vinylidene species [Ru(η^5-C_9H_7){=C=C(R)H}{κ^1(*P*)-$PPh_2(CH_2CH{=}CH_2)$}-(PPh_3)]$^+$ as the only intermediates observed.[11c] At about 30 min of reaction, the vinylidene species appears as the most abundant in solution with respect to both starting material and final product. Each vinylidene complex evolves further to give the bicyclic alkylidene compound. This has allowed us to treat independently the disappearance of complex **1** and that of the vinylidene intermediate and to obtain rate data for the [2 + 2] coupling process, as the second step of two consecutive reactions.[11a] The identification of vinylidene complexes as reaction intermediates has been confirmed by the independent synthesis and characterization of the tetrafluoroborate salts [Ru(η^5-C_9H_7){=C=C(R)H}-{κ^1(*P*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][BF_4] (R = Ph, (**3a**), *p*-MeC_6H_4 (**3b**)), which yield the corresponding bicyclic alkylidene products when kept in dichloromethane at reflux for 15 min.[11a] In the reaction of **1** with $Me_3SiC{\equiv}$CH, only the peaks of the starting material and of the product of [2 + 2] coupling, at δ 89.4 and 42.5 ppm ($^2J_{PP}$ = 32 Hz), are observed in the $^{31}P\{^1H\}$ NMR spectra. The trialkylsilyl substitution in the expected vinylidene intermediate renders such species very reactive, and therefore not detectable, with respect to the more stable aryl−vinylidene complexes. The reaction is accompanied by formation of a precipitate under the above experimental conditions, which has halted the kinetic study.

Rate Studies. Rate measurements have been performed for the reaction of complex **1** with PhC≡CH or *p*-$ClC_6H_4C{\equiv}CH$ toward the formation of the vinylidene species. In a series of $^{31}P\{^1H\}$ NMR spectra, the intensity of the low-frequency peak of complex **1** at −70.0 ppm ($PPh_2CH_2CH{=}CH_2$ resonance) decays exponentially until complete consumption, thus allowing us to calculate values of observed rate constants, k_{obs}. Figure 1 shows the disappearance of complex **1** (0.022 M) with time, in the presence of an excess of *p*-$ClC_6H_4C{\equiv}$CH (0.176 M), in which the solid line represents the best fit with the first-order rate equation (eq 2). The reaction

$$c_t = c_\infty + (c_0 - c_\infty)\exp(-k_{obs}t) \qquad (2)$$

is first order in complex **1**, and in this case, the calculated value of k_{obs} is 1.27 × 10^{-4} s^{-1}, implying a $\tau_{1/2}$ value of 90 min at 38.1 °C. Various experiments have been performed at different concentrations of PhC≡CH and *p*-$ClC_6H_4C{\equiv}CH$, and the values of k_{obs} are reported in Table 1. Figure 2 shows a plot of k_{obs} versus the concentration of the alkynes. In both cases, the linear dependence of k_{obs} on [alkyne] indicates the presence of a reaction pathway which is also first order in alkyne, overall second order, and the slopes of the lines yield the values of the corresponding rate constants, which are k_2 = [5.5(±0.4)] × 10^{-4} M^{-1} s^{-1} for phenylacetylene

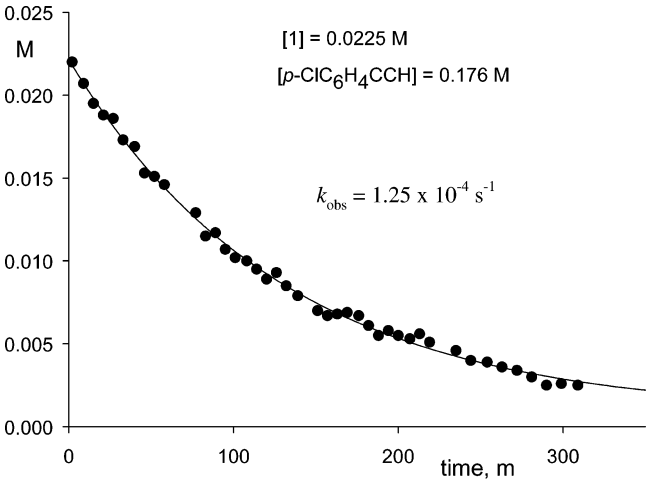


Figure 1. Plot of concentration values of complex **1** vs time for the reaction with *p*-$ClC_6H_4C{\equiv}CH$ in chloroform-*d* at 38.1 °C, as obtained by ^{31}P NMR. The experimental points are fitted with eq 2.

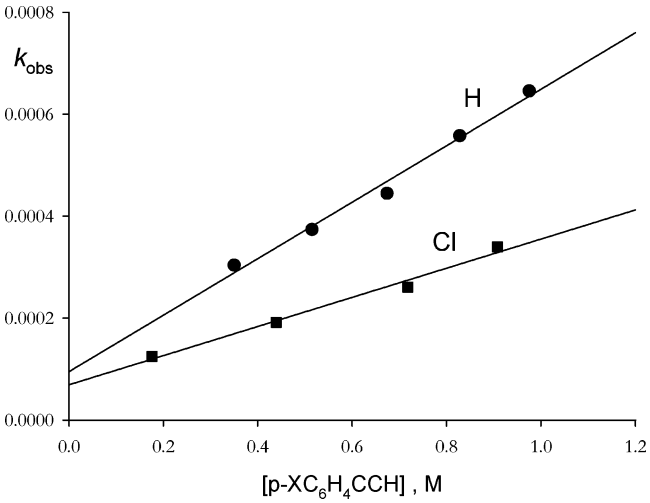


Figure 2. Plot of k_{obs} values for the reaction of [Ru(η^5-C_9H_7){κ^3(*P,C,C*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][PF_6] (**1**) with PhC≡CH (●) or *p*-$ClC_6H_4C{\equiv}CH$ (■), vs concentration of the alkyne, in chloroform-*d* at 38.1 °C.

(15) (a) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Martin-Vaca, B. M.; Anillo, A.; Tiripicchio, A. *Organometallics* **1992**, *11*, 1373−1381. (b) Braun, T.; Münch, G.; Windmüller, B.; Gevert, O.; Laubender, M.; Werner, H. *Chem. Eur. J.* **2003**, *9*, 2516−2530 and references therein.

Table 1. Values of Observed Rate Constants, k_{obs}, for the Reaction of [Ru(η^5-C_9H_7)-{κ^3(*P,C,C*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][PF_6] with PhC≡CH and *p*-$ClC_6H_4C{\equiv}CH$, in Chloroform-*d*, at 38.1 °C, Obtained from the Disappearance of Complex 1

[PhC≡CH], M	k_{obs}, 10^{-4} s^{-1}	[*p*-$ClC_6H_4C{\equiv}CH$], M	k_{obs}, 10^{-4} s^{-1}
0.350	3.04	0.176	1.25
0.515	3.74	0.439	1.92
0.674	4.45	0.718	2.61
0.828	5.58	0.908	3.40
0.975	6.46		

Table 2. Values of Kinetic Constants for the Reaction of [Ru(η^5-C_9H_7)-{κ^3(*P,C,C*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][PF_6] with Arylalkynes and with CD_3CN (L), in Chloroform-*d*, at 38.1 °C

L	k_1, s^{-1}	k_2, M^{-1} s^{-1}	R^a
PhC≡CH	[9.5(±2.5)] × 10^{-5}	[5.5(±0.4)] × 10^{-4}	0.994
p-$ClC_6H_4C{\equiv}CH$	[6.9(±1.5)] × 10^{-5}	[2.8(±0.3)] × 10^{-4}	0.993
CD_3CN[b]	1.5 (± 0.6) × 10^{-4}	[4.2(±0.2)] × 10^{-3}	0.998

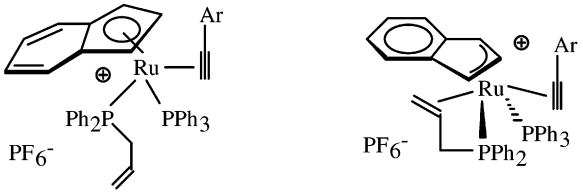
[a] Correlation coefficient. [b] Reference 14.

and [2.8(±0.3)] × 10^{-4} M^{-1} s^{-1} for *p*-chlorophenylacetylene. In addition, the positive value of the linear intercept on the *y* axis implies a contribution to k_{obs} arising from a pathway which is zero order in alkyne, overall first order, with the value k_1 = [9.5(±2.5)] × 10^{-5} s^{-1} for phenylacetylene and [6.9(±1.5)] × 10^{-5} s^{-1} for (*p*-chlorophenyl)acetylene (Table 2).[16] The latter values are the same within the experimental error, in agreement with the inferred zero-order dependence on the reagent. This situation is represented by the kinetic equation (3), which shows how the two pathways contribute to the observed reactivity.

$$k_{obs} = k_1 + k_2[\text{alkyne}] \qquad (3)$$

(a) Second-Order Pathway. The route represented by the second-order rate constant implies participation of both complex **1** and alkyne in the rate-determining step and can be regarded as an associative process, which is common in the reactions of indenyl complexes.[17] The higher reactivity often observed with respect to cyclopentadienyl analogues is explained in terms of favorable ring slippage of the indenyl ligand from an η^5 toward an η^3 coordination, upon attack of the nucleophilic reagent at the metal center.[18] We have reported that the insertion reactions of PhC≡CH and $(PhC{\equiv}C-)_2$ into the Ru−H bond of the complex [RuH(η^5-C_9H_7)(dppm)] (dppm = bis(diphenylphosphino)methane), with formation of the (*E*)-alkenyl complexes [Ru{(*E*)-CH=CHPh}(η^5-C_9H_7)(dppm)] and [Ru{(*E*)-CH(C≡CPh)=CHPh}(η^5-C_9H_7)(dppm)], proceed via an associative route, while no reaction is observed for the cyclopentadienyl complex [RuH(η^5-C_5H_5)(dppm)], as in a typical case of "indenyl effect".[19] Similar mechanistic features had been previously reported for the reaction of [IrH(η^5-C_9H_7)Me(PMe_3)] with *tert*-butylacetylene.[20] A mechanistic scheme involving the formation of an intermediate adduct between complex **1** and the alkyne is represented in Scheme 4.

Chart 1. Proposed Intermediate Adducts in the Second-Order Pathway of the Reaction between Complex 1 and ArC≡CH (Ar = Ph, *p*-ClC_6H_4)



Scheme 4

$$\mathbf{1} + \text{ArCCH} \underset{k_{-3}}{\overset{k_3\ (\text{slow})}{\rightleftharpoons}} \text{intermediate adduct} \xrightarrow{k_4} \text{vinylidene}$$

Inclusion of the corresponding rate equation into eq 3 yields eq 4.

$$k_{obs} = k_1 + k_2[\text{alkyne}] = k_1 + \frac{k_3 k_4[\text{alkyne}]}{k_{-3} + k_4} \qquad (4)$$

If the forward transformation of the adduct is faster than its reversal to the starting material ($k_4 \gg k_{-3}$), then the second-order rate constant k_2 corresponds to the formation of this intermediate from complex **1** and the alkyne (k_3). Therefore, the second-order pathway exhibited by complex **1** in the reactions of Scheme 2 should imply a rate-determining nucleophilic attack by the alkyne to induce either a ring slippage of the indenyl five-membered ring with formation of an η^3 intermediate species, or the displacement of the allylic double bond, according to a S_N2 mode. In fact, upon attack at the metal involving formation of the metal−π-alkyne bond, the metal complex can respond either by a haptotropic ring shift or by olefin dissociation. This slow step is followed by a fast 1,2-hydrogen shift within the η^2-alkyne species. According to this picture, Chart 1 shows the structures of the proposed intermediates in the second-order route. The nucleophilic character of the alkyne in this step is indicated by the greater reactivity of phenylacetylene with respect to (*p*-chlorophenyl)-acetylene.

(b) First-Order Pathway. A pathway which is zero order in alkyne implies rate-determining intramolecular rearrangement of complex **1** with formation of a transient intermediate, able to react rapidly in the following step with the alkyne. This is indicated by the fact that neither the concentration nor the nature of the alkyne influences the k_1 value. Due to its higher reactivity with

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(19) (a) Bassetti, M.; Casellato, P.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. *Organometallics* **1997**, *16*, 5470−5477. (b) Bassetti, M.; Marini, S.; Díaz, J.; Gamasa, M. P.; Gimeno, J.; Rodriguez-Álvarez, Y. *Organometallics* **2002**, *21*, 4815−4822.

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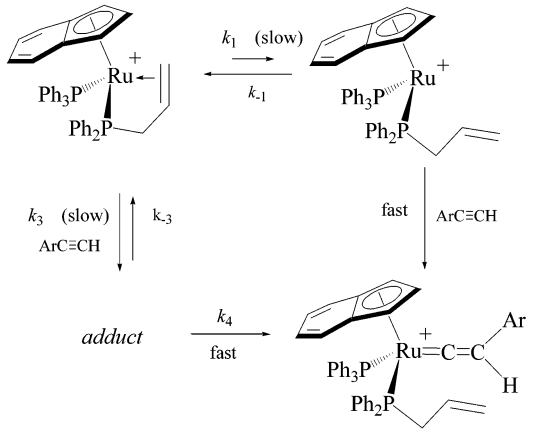
Scheme 5. Overall Mechanism of the Reaction of Complex 1 with Arylacetylenes



respect to complex **1**, this species reacts with the alkyne as soon as it forms and does not accumulate in the reaction medium. In light of the structure of complex **1**, in particular of the hemilabile character of the allylphosphine ligand, such a reactive intermediate may be regarded as arising from reversible dissociation of the allylic double bond, to yield the 16-electron species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]^+$. Such a species would form as a transient under steady-state conditions, being as such not detectable by spectroscopic means. In fact, it may either return to complex **1** by recoordination of the allylic double bond or react with the alkyne, both processes being rapid. The occurrence of an $\eta^5-\eta^3$ haptotropic equilibration of the indenyl ring as rate limiting along the first-order pathway can be reasonably excluded. In fact, rate-determining indenyl rearrangements only occur in the case of second-order reactions, when the reagent is part of the activated complex.[17−20] Another hypothesis compatible with the formation of a reactive species arising from complex **1** implies the release of PPh_3 to form the 16-electron species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}]^+$, in intermolecular equilibrium with the starting material. When complex **1** (0.012 M) was reacted with PhC≡CH (0.675 M) in the presence of an excess of PPh_3 (0.10 M), a k_{obs} value of 4.8×10^{-3} s^{-1} was found, which compares with the value $k_{obs} = 4.4 \times 10^{-3}$ s^{-1} observed in the absence of free phosphine. A rate depression should occur if rate-determining dissociation of PPh_3 plays any role along the first-order route. This result does not rule out the presence of a dissociative equilibrium of PPh_3 in complex **1** but indicates that it is not productive toward the activation of the alkyne molecule. The concept that the 16-electron bis(phosphine) intermediate $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]^+$ is reactive toward a terminal alkyne in the formation of a vinylidene species rather than the monophosphine species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}]^+$ agrees nicely with the fact that electron-rich ruthenium centers are required to assist the η^2-alkyne/η^1-vinylidene rearrangement.[1,3a]

A mechanistic description of the overall reactivity of complex **1** with terminal alkynes is represented in Scheme 5.

The first-order route would therefore arise from the reversible intramolecular dissociation of the allylic double bond from the metal center, a phenomenom indicated as "arm-off" mechanism.[12] It should be pointed out that observation of ligand hemilability by kinetic means is rare[21] and that the concept of kinetic detection of hemilability has been introduced only recently.[22] We have previously described that the reaction of complex **1** with nitriles yields the cationic complexes $[Ru(\eta^5\text{-}C_9H_7)(N{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ (R = Me, benzyl) by displacement of the double bond of allylphosphine.[14] The kinetics of the reaction with acetonitrile-d_3 have displayed the presence of parallel second- and first-order pathways, the latter taken as an indication of the occurrence of an arm-off mechanism of the allylphosphine system. At this stage, it should be considered that the rate of formation of the coordinatively unsaturated species $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]^+$, the y intercept in the plots, should be independent not only of the nature of the alkyne, as observed in the present study, but, in principle, also of the final destination of the complex, i.e., of the actual reaction in which it is involved. In agreement with this concept, the k_1 value found in the reaction of complex **1** with acetonitrile-d_3 ($(1.5 \pm 0.6) \times 10^{-4}$ s^{-1}) is within experimental error of the values found for the reaction with the arylacetylenes (Table 2), under identical conditions of solvent and temperature (see the graph in the Supporting Information).[23]

The second-order and first-order pathways in the reaction of complex **1** with alkynes can be regarded as parallel associative and dissociative routes, respectively. The contribution of the arm-off mechanism to the overall reactivity can be estimated from the graph of Figure 2, by comparison of the interpolated k_{obs} value at a chosen concentration of arylalkyne with the corresponding k_1 value. For instance, at $[p\text{-}XC_6H_4C{\equiv}CH] \cong 0.5$ M, the reaction proceeds via the first-order pathway to an extent of about 25% (X = H) and 33% (X = Cl), respectively. The contribution of the arm-off mechanism becomes relatively large at low concentration of alkyne and smaller at increasing values. While associative reactions are typical of indenyl complexes, some cases have also been reported of ligand substitution reactions which occur by dissociative mechanisms.[24] In particular, we have reported that the exchange of triphenylphosphine in the complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with phosphines of smaller cone angle proceeds exclusively by rate-determining PPh_3 dissociation and that the indenyl complex reacts 1 order of magnitude faster than the corresponding cyclopentadienyl analogue.[25] Mixed associative and dissociative modes for substitution reactions in indenyl complexes have also been reported.[26]

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(23) The larger reactivity of acetonitrile-d_3 with respect to the arylacetylenes in the second-order pathway corresponds to a steeper slope of the line in the graph of k_{obs} vs concentration of the reagent, implying a larger error in the estimate of the y intercept.[14]

(24) (a) Jones, D. J.; Mawby, R. J. *Inorg. Chim. Acta* **1972**, *6*, 157−160. (b) Pevear, K. A.; Banaszak Holl, M. M.; Carpenter, G. B.; Rieger, A. L.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1995**, *14*, 512−523.

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Conclusions

This work reports a kinetic investigation of the reaction of terminal alkynes with a ruthenium indenyl complex bearing an hybrid allylphosphine ligand to yield η^1-vinylidene derivatives. The study does not give information about the η^2-alkyne/η^1-vinylidene transformation at the metal center (Scheme 1), which has been previously investigated in various ruthenium systems, but discloses the interactive modes of the metal complex with the incoming alkyne molecule. The 18-electron complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ reacts via parallel pathways, one characterized by rate-determining bimolecular interaction with the alkyne and one involving intramolecular rate-determining dissociation of the allylic double bond to form a transient 16-electron intermediate. The proposed arm-off mechanism regarding the allylphosphine ligand finds in this work a sound experimental support, since it has been found to be independent of the alkyne structure and also of the specific reaction involved. The data here presented along with those from the reaction of complex **1** with nitriles represent the first case of detection and quantitative evaluation by kinetic means of the hemilability of a hybrid olefin−phosphine ligand.

Experimental Section

General Conditions. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)]$,[27] $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3\text{-}(P,C,C)\text{-}PPh_2P(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$,[14] and $PPh_2P(CH_2\text{-}CH{=}CH_2)$[28] were prepared by previously reported methods. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT or a Perkin-Elmer 599 IR spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B micro analyzer. NMR spectra were recorded on Bruker AC300 or 300DPX instruments at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard. DEPT experiments have been carried out for all the compounds. Coupling constants *J* are given in hertz. ADPP is allyldiphenylphosphine.

Synthesis of $[Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}CR\}\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$ (R = Ph (2a), *p*-MeC_6H_4 (2b), *p*-ClC_6H_4 (2c)). Method a. A mixture of $[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^1(P)\text{-}Ph_2P(CH_2CH{=}CH_2)\}(PPh_3)]$ (0.44 g, 0.45 mmol) and the corresponding terminal alkyne (2.7 mmol) in MeOH (25 mL) was heated until complete dissolution of the ruthenium complex occurred. Afterward, KOH (0.06 g, 1.2 mmol) was added and the mixture was refluxed for 45 min. The solvent was removed under vacuum, and the resulting solid was purified by chromatographic column, recovering the fraction eluted with diethyl ether. Evaporation of the solvent afforded the yellow solid $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)]$ in 80−90% yield.

Method b. To a solution of $[Ru(\eta^5\text{-}C_9H_7)Cl\{\kappa^1(P)\text{-}PPh_2\text{-}(CH_2CH{=}CH_2)\}(PPh_3)]$ (0.75 g, 1 mmol) in CH_2Cl_2 at reflux (10 mL) were added phenylacetylene or *p*-tolylacetylene (2 mmol) and KO*t*Bu (0.11 g, 1 mmol). The mixture was refluxed for 10 min to form an orange solution. Solvents were then evaporated, and the resulting solid was extracted with CH_2Cl_2 (2 × 10 mL). The solution was evaporated to dryness to afford an orange solid which was purified on a chromatographic column, recovering the fraction eluted with diethyl ether, to afford the complex $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CR)\{\kappa^1(P)\text{-}PPh_2P(CH_2CH{=}CH_2)\}(PPh_3)]$ in 85−90% yield. R = Ph (**2a**): 85% yield. Anal. Calcd for $C_{50}H_{42}P_2Ru$: C, 74.51; H, 5.25. Found: C, 74.99; H, 5.61. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.5 (d, J_{PP} = 31.7 Hz, PPh_3), 44.1 ppm (d, J_{PP} = 31.7 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 1.98 (m, 2H, CH_2), 2.37 (m, 1H, CH_2), 3.97 (m, 1H, =CH_2), 4.49 (s, 1H, H1), 4.61 (m, 1H, =CH_2), 4.71 (m, 1H, =CH), 4.99 (s, 1H, H3), 5.49 (s, 1H, H2), 6.41−8.12 ppm (m, 34H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.1 (d, J_{CP} = 27.2 Hz, CH_2), 75.8 (s, C1, 3), 89.9 (br s, Cα), 97.8 (s, C2), 109.8 (s, Cβ), 111.0 (s, C3a, C7a), 115.7 (s, C3a, C7a), 119.8 (d, J_{CP} = 8.4 Hz, =CH_2), 123.2 (s, =CH), 127.0−142.0 ppm (m, Ar). R = *p*-MeC_6H_4 (**2b**): 90% yield. Anal. Calcd for $C_{51}H_{44}P_2Ru$: C, 74.70; H, 5.40. Found: C, 74.38; H, 5.50. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.2 (d, J_{PP} = 31.7 Hz, PPh_3), 43.5 ppm (d, J_{PP} = 31.7 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 1.85 (m, 1H, CH_2), 2.38 (s, 3H, Me), 2.45 (m, 1H, CH_2), 3.56 (m, 1H, =CH_2), 4.34 (s, 1H, H1), 4.45 (m, 1H, =CH_2), 4.57 (m, 1H, =CH), 4.85 (s, 1H, H2), 5.31 (s, 1H, H3), 6.30−8.11 ppm (m, 33H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (s, Me), 31.8 (d, J_{CP} = 31.2 Hz, CH_2), 73.9 (d, J_{CP} = 20.5 Hz, Cα), 79.4 (d, J_{CP} = 5.6 Hz, C1), 84.3 (d, J_{CP} = 7.8 Hz, C3), 92.9 (s, Cβ), 99.8 (s, C2), 113.8 (s, C3a, C7a), 114.5 (s, C3a, C7a), 121.9 (s, =CH_2), 127.5 (s, =CH), 127.0−140.0 ppm (m, Ar). R = *p*-Cl (**2c**): 90% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.4 (d, J_{PP} = 32.0 Hz, PPh_3), 44.2 ppm (d, J_{PP} = 32.0 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 1.96 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 3.90 (m, 1H, =CH_2), 4.46 (s, 1H, H1), 4.62 (m, 1H, =CH_2), 4.57 (m, 1H, =CH), 4.99 (s, 1H, H2), 5.31 (s, 1H, H3), 6.30−8.11 ppm (m, 33H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.9 (s, br, CH_2), 74.1(s, C1), 79.4 (s, C3), 92.0 (br s, Cα), 95.4 (s, C2), 107.6 (s, C3a, C7a), 108.6 (s, C3a, C7a), 113.5 (s, Cβ), 118.2(s, =CH_2), 122.5 (s, =CH), 124.0−139.5 ppm (m, Ar). IR (Nujol): 1055 (BF_4), 1632 (C=C) cm^{-1}. No analytically pure samples were obtained.

Synthesis of $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(R)H\}\{\kappa^1(P)\text{-}PPh_2(CH_2\text{-}CH{=}CH_2)\}(PPh_3)][BF_4]$ (R = Ph (3a), *p*-MeC_6H_4 (3b)). A stirred solution of the alkynyl complexes **2a**−**c** (1 mmol) in diethyl ether (20 mL), at room temperature, was treated dropwise with a dilute solution of $HBF_4{\cdot}Et_2O$ in diethyl ether (ca. 7%). Immediately, an insoluble solid precipitated. The addition was continued until no further solid was formed (ca. 3 mL). The resulting brown solid was recovered by filtration, washed with diethyl ether (3 × 20 mL), and vacuum-dried. R = Ph (**3a**): 80% yield. Anal. Calcd for $C_{50}H_{43}BF_4P_2Ru$: C, 67.19; H, 4.84. Found: C, 66.85; H, 4.51. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.4 (d, J_{PP} = 23.9 Hz, PPh_3), 32.4 ppm (d, J_{PP} = 23.9 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 2.81 (m, 2H, CH_2), 4.32 (m, 1H, =CH_2), 4.58 (m, 1H, =CH_2), 4.82 (m, 1H, =CH), 5.34 (br s, =C=CH), 5.61 (s, 1H, H1), 5.65 (s, 1H, H3), 5.82 (s, 1H, H2), 6.51−7.9 ppm (m, 34H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.9 (d, J_{CP} = 31.6 Hz, CH_2), 81.3 (s, C1), 85.8 (s, C3), 100.9 (s, C2), 114.2 (s, C3a, C7a), 115.7 (s, C3a, C7a), 116.1 (s, Cβ), 120.1 (d, J_{CP} = 20.0 Hz, =CH), 121.9 (s, C_9H_7), 123.2 (d, J_{CP} = 27.4 Hz, =CH_2), 125.1 (s, C_9H_7), 126.0−138.2 (m, Ar), 360.1 ppm (s, br, Cα). IR (Nujol): 1063 (BF_4), 1628 cm^{-1} (=C=C). R = *p*-MeC_6H_4 (**3b**): 95% yield. Anal. Calcd for $C_{51}H_{45}BF_4P_2$-Ru: C, 67.48; H, 4.99. Found: C, 67.11; H, 4.76. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.6 (d, J_{PP} = 25.4 Hz, PPh_3), 32.2 ppm (d, J_{PP} = 25.4 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 2.31 (s, Me), 2.82 (m, 2H, CH_2), 4.29 (m, 1H, =CH_2), 4.57 (m, 1H, =CH_2), 5.12 (m, 1H, =CH), 5.31 (br s, =C=CH), 5.52 (s, 1H, H1), 5.61 (s, 1H, H2), 5.71 (s, 1H, H3), 6.21−7.93 (m, 33H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.2 (d, J_{CP} = 13.6 Hz, Me), 32.9 (d, J_{CP} = 28.7 Hz, CH_2), 80.8 (d, J_{CP} = 9.6 Hz, C1), 85.8 (s, C3), 100.9 (s, C2), 112.8 (s, C3a, C7a), 114.2 (s, C3a, C7a), 117.2 (s, Cβ), 120.2 (d, J_{CP} = 21.3 Hz, =CH), 122.9 (s, C_9H_7), 123.7 (d, J_{CP} = 27.0 Hz, =CH_2), 125.3 (s, C_9H_7), 126.0−139.9 (m, Ar), 369.2 ppm (br s, Cα). IR (Nujol): 1055 (BF_4), 1632 cm^{-1} (=C=C).

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Synthesis of [Ru(η^5-C_9H_7){=C=C(R)Me}{κ^1(*P*)-PPh_2-(CH_2CH=CH_2)}(PPh_3)][BF_4] (R = Ph (4a), *p*-MeC_6H_4 (4b)). A stirred solution of the alkynyl complexes **2a**,**b** (1 mmol) in diethyl ether (20 mL), at room temperature, was treated dropwise with a dilute solution (ca. 5%) of $MeOSO_2CF_3$. Immediately, an insoluble solid precipitated. The addition was continued until no further solid was formed. The solvents were decanted, and the resulting solid was recrystallized from CH_2Cl_2/diethyl ether and vacuum dried. R = Ph (**4a**): yield 85%. Anal. Calcd for $C_{52}H_{45}F_3O_3P_2RuS$: C, 64.38; H, 4.67. Found: C, 63.97; H, 4.44.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.4 (d, J_{PP} = 24.4 Hz, PPh_3), 32.2 ppm (d, J_{PP} = 24.4 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H, Me), 2.51 (m, 2H, CH_2), 4.21 (m, 1H, =CH_2), 4.52 (m, 1H, =CH_2), 4.73 (m, 1H, =CH), 5.32 (s, 1H, H1), 5.45 (s, 1H, H3), 5.73 (s, 1H, H2), 6.01−7.70 ppm (m, 34H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.3 (s, Me), 32.5 (d, J_{CP} = 29.9 Hz, CH_2), 81.4 (s, C1), 83.2 (s, C3), 97.7 (s, C2), 111.4 (s, C3a, C7a), 111.6 (s, C3a, C7a), 117.3 (s, Cβ), 120.1 (d, J_{CP}=20.0 Hz, =CH), 122.3 (d, J_{CP} = 25.6 Hz, =CH_2), 127.0−142.0 (m, Ar), 347.6 ppm (t, J_{CP} = 21.5 Hz, Cα). IR (Nujol): 1198 (CF_3SO_3), 1641 cm^{-1} (=C=C). R = *p*-MeC_6H_4 (**4b**): yield 90%. Anal. Calcd for $C_{53}H_{47}F_3O_3P_2RuS$: C, 64.69; H, 4.81. Found: C, 64.38; H, 5.01. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.5 (d, J_{PP} = 26.4 Hz, PPh_3), 32.5 ppm (d, J_{PP} = 26.4 Hz, ADPP). ^1H NMR ($CDCl_3$): δ 1.92 (s, 3H, Me), 2.42 (s, 3H, Me), 2.61 (m, 2H, CH_2), 4.25 (m, 1H, =CH_2), 4.55 (m, 1H, =CH_2), 4.70 (s, 1H, =CH), 5.41 (s, 1H, H1), 5.69 (s, 1H, H3), 5.89 (s, 1H, H2), 6.10−7.66 ppm (m, 33H, Ar H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.6 (s, Me), 21.1 (s, Me), 32.1 (d, J_{CP} = 27.6 Hz, CH_2), 81.5 (s, br, C1), 83.2 (br s, C3), 98.3 (s, C2), 112.1 (s, C3a, C7a), 117.0 (s, C3a, C7a), 119.9 (d, J_{CP} = 20.0 Hz, =CH), 121.9 (s, Cβ), 123.2 (d, J_{CP} = 25.6 Hz, =CH_2), 124.3 (s, C_9H_7), 126.0−138.2 (m, Ar), 348.4 ppm (br s, Cα). IR (Nujol): 1203 (CF_3SO_3), 1639 cm^{-1} (=C=C).

Kinetic Measurements. ^1H and ^{31}P NMR spectra were obtained using a Bruker AC 300 P instrument. Manipulations were performed under argon. A weighed amount of complex **1** (11−13 mg) was dissolved in chloroform-*d* (0.500 mL) into a 5 mm NMR tube, and the appropriate amount of alkyne was added using a microsyringe in the case of PhC≡CH or Me_3SiC≡CH or as a weighed solid in the case of *p*-ClC_6H_4-C≡CH. The samples were shaken to obtain clear solutions just before introduction into the NMR probe, and the experiment was started immediately afterward, after allowing about 1 min for thermal equilibration and experiment setup. A macro sequence of the Aspect 3000 software was used for the collection of fids at regular interval times, each one with identical acquisition parameters. The observed rate constants for consumption of complex **1** were obtained from nonlinear least-squares regression analysis by fitting the exponential dependence of concentration, *c*, calculated from the peak intensities of the $^{31}P\{^1H\}$ NMR resonance of complex **1** at −70.0 ppm, against time, according to the first-order rate equation (eq 2). The procedure yields values of c_∞, k_{obs}, and correlation coefficient (*R*), which were ≥0.99. The k_{obs} values were checked against those obtained from straight-line plots of ln *c* vs time and found to be in good agreement.

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Note Added after ASAP. Due to a production error, the version of the paper that was published on the Web on Sept. 30, 2004, contained errors in some of the chemical formulas. The version that now appears is correct.

Supporting Information Available: A figure giving a plot of k_{obs} values for the substitution reaction of complex **1** with CD_3CN and for the reactions of complex **1** with PhC≡CH and *p*-ClC_6H_4C≡CH. This material is available free of charge via the Internet at http://pubs.acs.org.

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